

workers⁵ to suggest that below 1°K liquid He³ must undergo a transition to account for this excess entropy or there may be a hump in the heat capacity. In the absence of further experimental data below 1°K, it would be hard to say anything regarding the nature of this transition, yet it is not without interest to speculate on its nature. It is possible to account for this excess entropy on the basis of the following phenomenological picture. The liquid phase, presumably, near 1°K goes into a peculiar ordered state resembling somewhat a loose solid. It is a sort of a λ -transition. The specific heat of this ordered phase is no longer given by (2b) but by the Debye expression

$$C_v = 464.5 (T/\theta)^3 \text{ cal mole}^{-1} \text{ deg}^{-1}, \quad (4)$$

which gives

$$S = (C_v/T)dT = \frac{1}{3} \cdot 464.5(T/\theta)^3 \text{ cal mole}^{-1} \text{ deg}^{-1}. \quad (5)$$

Using Eq. (5) and assuming that the λ -transition takes place at 1°K, we can explain the residual entropy if the value of the characteristic temperature θ is taken as 4.3°K. Expression (4) includes the contribution of both the transverse and the longitudinal waves; and if we assume that it is only the latter which contribute we shall require θ to be smaller still. One would like to ask whether such a low value of θ is compatible with our knowledge about He⁴. Recently Kramers⁸ has reported that, below 0.6°K, the specific heat of He⁴II can be roughly represented by a T^3 law, with $\theta \approx 27^\circ\text{K}$, in agreement with Landau's theoretical estimate which excludes the transverse waves. The characteristic temperature θ of solid He⁴, as has been pointed out by Simon,⁹ varies markedly with density. If the density changes by a factor 2, θ changes by a factor of 4. The observed density of liquid He⁴ near the absolute zero is roughly twice the observed density of liquid He³ at the same temperature. We, therefore, expect that for liquid He³ θ will be about 7°K, if not smaller. If we use London's expression¹⁰ to calculate the zero-point energy of He³ corresponding to $\rho = 0.8 \text{ g/cc}$, we find that $u_0 = 18 \text{ cal mole}^{-1}$, giving $\theta = 8^\circ\text{K}$. Thus a low value of θ is quite compatible with this theory. However, to account for the excess entropy of liquid He³, we shall have to assume a value of θ about half the theoretically expected value.

It may be worth pointing out that a jump, if there is any, in the specific heat should show up as an angular point in the heat of vaporization *versus* temperature curve. No such jump is evident in the curve given by Abraham and co-workers.⁶ It would be of great theoretical interest to extend the experimental investigation of the heat of vaporization below 1°K.

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- ¹¹ *Note added in proof.*—After this letter was submitted for publication, the author received from Dr. L. Goldstein of Los Alamos Scientific Laboratory his unpublished calculations on the entropy and specific heat of He³, which agree with those of the author. Dr. Goldstein does not consider the residual entropy.

Magnetic Shielding Effects in Compounds of Vanadium*

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RECENT measurements to determine the gyromagnetic ratio of vanadium 50¹ in VOCl₃ and inconsistencies in the reported values²⁻⁴ for vanadium 51 led to the desirability of checking for shifts due to magnetic shielding. Since V⁵⁰ enriched com-

TABLE I. Nuclear resonance data for vanadium compounds.

Compound	Valence	Observed line width in gauss ^a	$\nu(\text{V}^{51})/\nu(\text{Na}^{23})$	% field shift
NaVO ₃	+5	0.35	0.993855 ± 0.000025	0.00
Na ₂ VO ₄	+5	0.35		
NH ₄ VO ₃	+5	0.35		
VO(NO ₃) ₂	+4	2.3	0.993855 ± 0.000035	0.00
VO(SO ₄)	+4	1.1		
K ₂ V ₄ O ₉	+4	1.4		
V ₂ O ₅ powder	+5	10.1		
VCl ₂	+2	2.0		
VOCl ₂	+4	1.5		
Pb(VO ₃) ₂	+5	~16.1		
VOCl ₃	+5	0.25	0.994358 ± 0.000026	-0.05
V metal (powder)	...	8.5	0.999960 ± 0.00001	-0.61

^a $H^* = 6740$ gauss, frequency = 7550 kc.

pounds were not readily available and the signal of V⁵⁰ is extremely weak in natural concentration (0.25 percent), compounds of V⁵¹ in normal abundance were used for all measurements. The nuclear magnetic resonance for V⁵¹ was observed in VOCl₃, and the measured value was found to differ from those previously reported for other compounds.²⁻⁴ The metal powder and several compounds of V⁵¹ were then investigated and data are reported in Table I. Accurate frequency measurements were made with reference to sodium for the NaVO₃, VOCl₃, and V metal resonances. Other compounds were measured relative to the vanadium resonance in VOCl₃. The signal from solid Pb(VO₃)₂ was too broad for accurate determination of the resonance frequency. No signals were observed for V₂O₅, VOF₃, or VF₃, all in the solid state. All resonances were measured in saturated aqueous solutions except for VOCl₃ (liquid at room temperatures), V₂O₅, and Pb(VO₃)₂ (both dry powders). Care was exercised in the preparation of the chemical compounds to eliminate effects of possible admixtures. This was necessary since a great many of the vanadium compounds are unstable or decompose under the effects of light and heat. No magnetic catalysts were added to the samples.

All measurements were made at an identical position in the magnetic field. In cases where two compounds could not be mixed because of chemical considerations, one was sealed in a small spherical glass vial of 0.2-ml volume and the vial surrounded with the other compound. Magnetic field homogeneity over the entire coil volume is such that resonances have been observed with signal widths as narrow as 0.2 gauss. The shifts observed were at least 15 times this amount. The width of the signal resonance is given for points of maximum deflection of the derivative of the absorption curve for the value of magnetic field H^* at which the signal was observed. Our value for the line width of the metallic vanadium is smaller than that reported by Knight.⁵ There appears to be no correlation of the shift observed for VOCl₃ with the valence state or the bonding orbitals in this molecule.

The resonance occurring at the highest value of externally applied field exhibits the least paramagnetic shielding.^{6,7} Also, it has been shown⁸ that the percent shift to be expected for different isotopes is the same for similar compounds of those isotopes. Thus, a small correction can be made in the data reported for V⁵⁰.¹ In addition, we report a direct measurement of the ratio of V⁵¹ in the two compounds VOCl₃ and NaVO₃. Using this value, the earlier value for V⁵⁰, the sodium-to-proton frequency ratio of 0.264518,^{9,10} and the deuterium-to-proton frequency ratio of 0.1535059,¹¹ we report final values as listed in Table II.

The signs of both magnetic moments have been determined to be positive by comparison with known elements and are in agree-

TABLE II. Frequency ratios for vanadium isotopes.

$\nu(\text{V}^{51})/\nu(\text{V}^{50})$ in (NaVO ₃ /VOCl ₃)	0.999491 ± 0.000010
$\nu(\text{V}^{50})/\nu(\text{D}_2)$ in (NaVO ₃)	0.649203 ± 0.000012
$\nu(\text{V}^{50})/\nu(\text{V}^{51})$ in (VOCl ₃)	0.379074 ± 0.000017

ment with that reported for V^{51} by Proctor and Yu.⁴ The spin for V^{50} is as yet undetermined; however, the Mayer shell model¹² predicts both odd nucleons to be in the $2F_{7/2}$ states. If the spins are assumed to be additive, the compound nuclear magnetic moment (uncorrected) becomes $+3.898$ nuclear magnetons. Using a diamagnetic correction of 0.171 percent,¹³ the corrected value becomes $\mu(V^{50}) = +3.905$ n.m., which may be compared with the $j-j$ coupling value of 3.85 n.m. as computed from data given by Feenberg.¹⁴

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Lifetime of an Excited State of Hf^{176}

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AN excited state in Hf^{176} with a half-life $(1.35 \pm 0.10) \times 10^{-9}$ sec has been observed with a delayed coincidence scintillation spectrometer using sources of Lu^{176} . The isomeric transition is classified $E2$ by a measurement of the K -shell internal conversion coefficient.

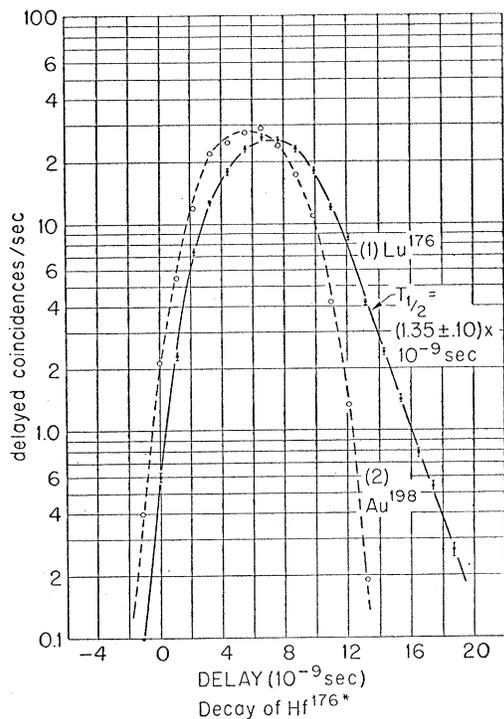


Fig. 1. Delayed coincidences as a function of the delay time.

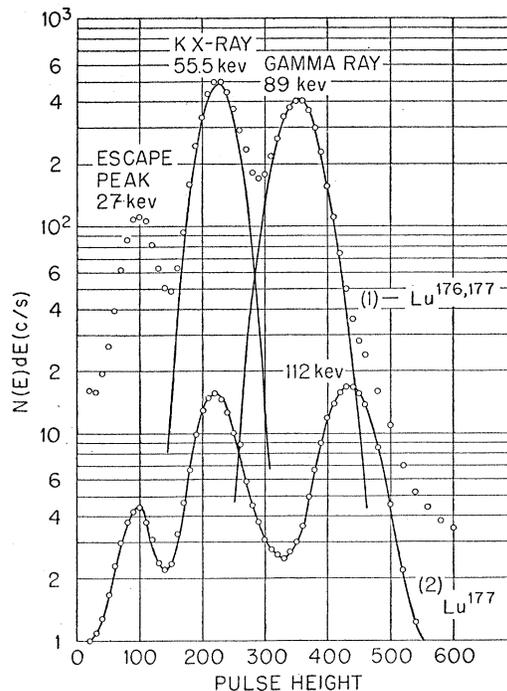


Fig. 2. Spectrum of the γ -radiation following the β^- decay of Lu^{176} .

Lu^{176} (3.75 hr) is known¹ to decay by two beta-ray groups into Hf^{176} . The softer beta-ray group is followed by an 89-keV γ -ray.

Curve (1) of Fig. 1 shows the number of coincidences as a function of the delay time with a source of Lu^{176} . This delayed coincidence resolution curve was recorded by exciting one channel of the delayed coincidence apparatus by 250- to 400-keV nuclear beta-rays and the other channel by the L , M , or N internal conversion electrons of the 89-keV transition.

A resolution curve for prompt events was obtained with a source of Au^{198} . The prompt coincidences were (a) between 50 to 110 keV nuclear beta-rays and the internal conversion electrons of the 411-keV transition, and (b) between 50- to 110-keV Compton recoil electrons and 250- to 400-keV nuclear beta-rays. Curve (2) of Fig. 1 shows the result of such a measurement. Thus, for delay $T \geq 12 \times 10^{-9}$ sec the half-life of Hf^{176} may be determined from the slope of curve (1).

The K -shell internal conversion coefficient of the 89-keV transition was obtained from a spectral measurement of the γ -radiation following the beta-decay of Lu^{176} . A typical spectrum of the K x-ray and the 89-keV γ -ray obtained with an NaI scintillation spectrometer is shown in Fig. 2. Curve (1) is the spectrum of the γ -radiation from Lu^{176} plus Lu^{177} (6.7 days) which is present in the source. Curve (2) is the contribution of Lu^{177} to the spectrum. The intensity ratio of the K x-ray to the γ -ray is obtained from the observed spectrum provided the appropriate corrections are made for fluorescent yield, effective detection efficiency, and escape peak intensities. The result for α_{exp}^K is 1.25 ± 0.15 .

The extrapolated K -shell internal conversion coefficients² for electric dipole, quadrupole, and magnetic dipole are $\alpha_1^K = 0.40$, $\alpha_2^K = 1.35$, and $\beta_1^K = 6.1$. Thus, the transition is of the $E2$ type and the spin of the metastable state is two. Scharff-Goldhaber, der Mateosian, and Mihelich¹ reached this conclusion from a measurement of the K/L conversion ratio. This is another example of the rule that the first excited state in even-even nuclei has spin 2 and even parity, assuming even parity for the ground state as seems likely by the shell model.

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